Dehydration of 3,3′,4,4′-benzophenone tetracarboxylic acid into its dianhydride

Ye Su [a], Zhou Dezhen [b] and Wei Jingxiang [b]

[a] *Research Institute for Chemical Processing and Utilization of Forest Products, Chinese Academy of Forestry, Nanjing, Jiangsu Province 210037 (People's Republic of China)*
[b] *Liming Research Institute for Chemical Industry, Luoyang, Henan Province 471001 (People's Republic of China)*

(Received 20 March 1991)

Abstract

The dehydration of 3,3′,4,4′-benzophenone tetracarboxylic acid (BTA) into its dianhydride (BTDA) has been studied by TG–DSC methods. The influences of reaction conditions on the purity of BTDA are discussed. Using isothermal TG data, kinetic analysis of the dehydration reaction has been made by a sequential procedure. The one-dimensional diffusion model ($X^2 = Kt$) is found to be the best for the kinetic equations examined. The kinetic parameters are calculated. The optimal dehydration temperature is in the approximate range 182–211°C. When the dehydration temperature is higher than the melting point of BTDA, it degrades significantly. The extent of degradation chiefly depends on the temperature and scarcely bears any relation to the atmosphere.

INTRODUCTION

3,3′,4,4′-Benzophenone tetracarboxylic dianhydride (BTDA) is a multi-functional compound containing two aromatic nuclei; therefore, it is widely used for the manufacture of heat resistant polymers, such as polyamides and polyimides. BTDA is prepared generally by means of the dehydration of the corresponding acid 3,3′,4,4′-benzophenone tetracarboxylic acid (BTA). Concerning the dehydration process, little has been investigated in detail; moreover, the dehydration kinetics have not been reported until now. If BTDA contains some coloured impurities produced during the reaction, it would lead to a low degree of condensation polymerization and seriously influence the quality of final polymer products. Therefore, the object of this work was to investigate the influences of reaction conditions on the purity of BTDA and kinetics of dehydration of BTA.

EXPERIMENTAL

BTA used in this study was supplied by the Liming Research Institute for Chemical Industry. It was a light yellow powder having greater than 99% purity and an acid number of 626 mg KOH g^{-1}.

For both the isothermal and dynamic measurements, a Rigaku Standard Micro TG–DTA thermal analyzer was used. Experiments for dehydration kinetics were carried out on a Perkin Elmer TG-2 thermobalance. The sample mass was 5 mg and the heating rate was $10°C$ min^{-1}, unless otherwise stated. The purity of nitrogen used was greater than 99.99%. Infrared spectra were recorded using a Perkin Elmer 580 B spectrophotometer on KBr plate.

RESULTS AND DISCUSSION

Influences of reaction conditions on purity of resulting BTDA

A set of typical TG–DSC curves of BTA is illustrated in Fig. 1. The endothermic peak at the maximum temperature of 240°C in DSC corresponds to the weight loss in the 182–256°C range in TG. The IR analysis for the samples before and after the reaction demonstrate that BTA has changed into BTDA (see Fig. 2). Thereafter, the DSC curves drift progres-
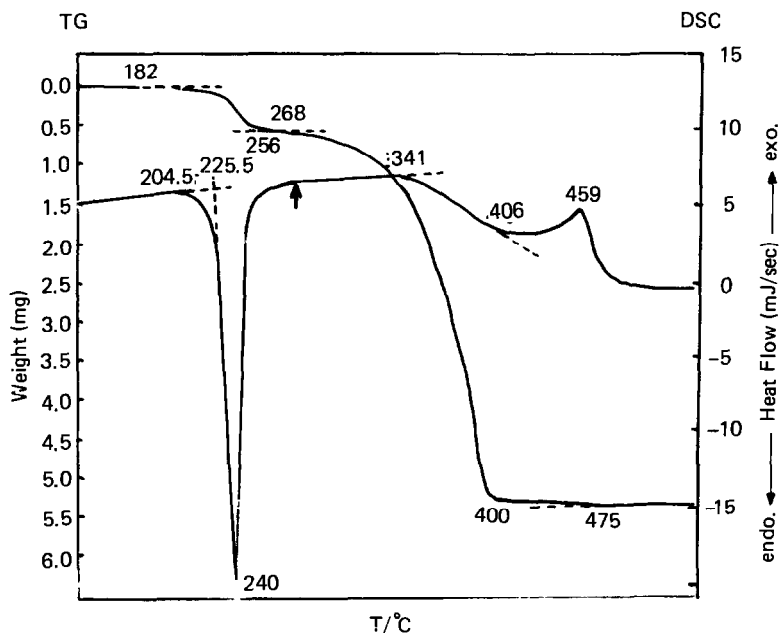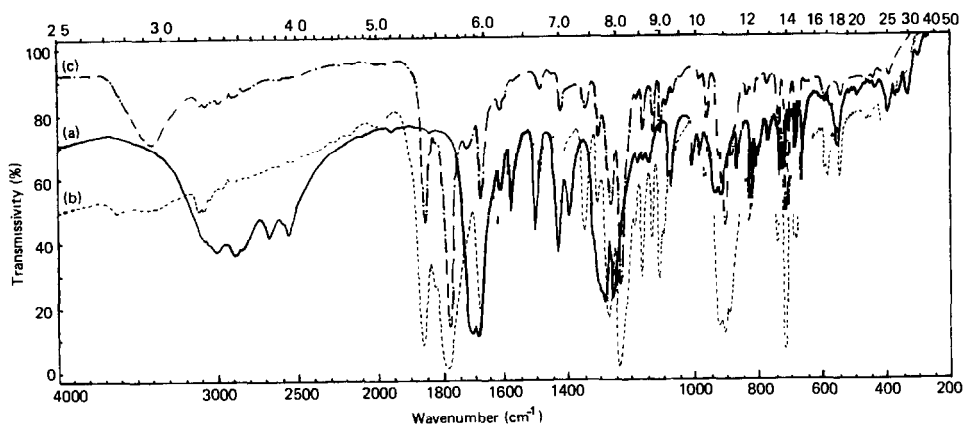

Fig. 1. TG–DSC curves of BTA at $10°C$ min^{-1}.

Fig. 2. IR spectra of BTA before and after heating: (a) ———, unheated; (b) ······, heated to 275°C; (c) –·–·–, after isothermal weight loss at 203°C for 1 h.

sively to the endothermic side and accompany obvious weight loss, due to the evaporation of melting BTDA. At this moment some white crystal can be collected from the inside wall of the furnace cover which has been confirmed to be BTDA from its IR spectrogram. The final exothermic phenomenon is possibly produced by air oxidation and decomposition of residual BTDA.

From the TG–DSC curves of BTA at various heating rates given in Fig. 3, it can be seen clearly that the endothermic peak at 240°C in Fig. 3(a) divides gradually into two peaks as the heating rate decreases. At 1.25 and 0.625°C min^{-1} they separate totally. The former endothermic peak (A) accompanies a weight loss, while for the following peak (B), the maximum temperature is 224°C and no weight loss is observed. When BTA is heated at 0.625°C min^{-1} to just the end of peak A and then cooled, the product is a light yellow powder which has a melting point of 225°C; this is in good agreement with peak B in Figs. 3(d) and 3(e). Its IR spectrum is the same as that of BTDA reported in IR Sadler standard spectra.

Through statistical analysis the weight loss of the sample is found to be equal to the weight corresponding to the elimination of two moles of water per mole of BTA. From these results, it may be concluded that peak A is attributable to the dehydration of BTA, while peak B is due to the melting of BTDA. The equation of dehydration is shown in Scheme 1.

The melting points of BTA reported in the literature are not quite consistent [1,2]. The above experiments show that BTA has undergone dehydration before melting at ordinary pressure. When the heating rate is slower, the value observed is the melting point of BTDA formed in the substance, but when it is faster, the dehydration of BTA and the melting of BTDA take place simultaneously. This study found for BTDA, m.p. 224.8 ± 0.6°C, heat of melting 29.1 ± 1.3 KJ mol^{-1}, and heat of dehydration of
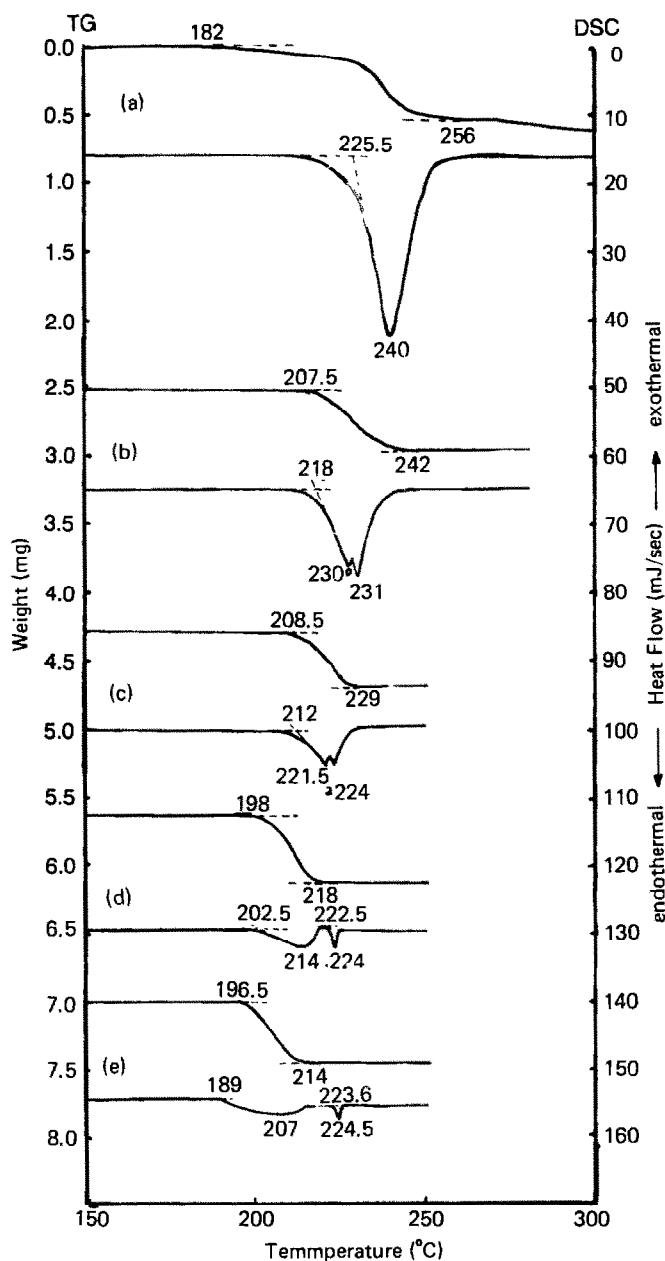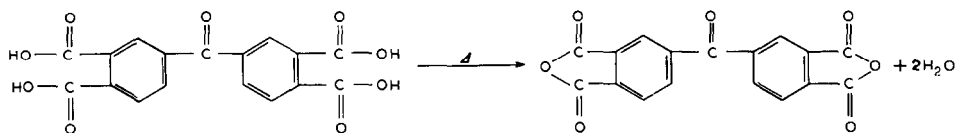
Fig. 3. TG–DSC curves of BTA at various heating rates: (a) $10\,^{\circ}C$ min^{-1}, (b) $5\,^{\circ}C$ min^{-1}, (c) $2.5\,^{\circ}C$ min^{-1}; (d) $1.25\,^{\circ}C$ min^{-1}; (e) $0.625\,^{\circ}C$ min^{-1}.

BTA 64.1 ± 7.5 KJ mol^{-1} (peak areas were measured by the paper weight method).

The plot of dehydration temperature versus heating rate was extrapolated to zero heating rate. The optimal dehydration temperature is reckoned
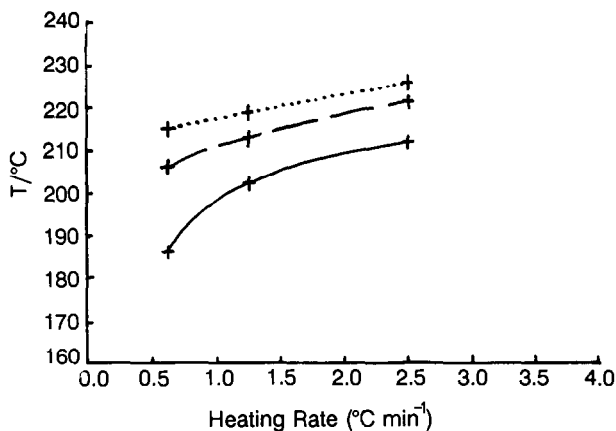
Scheme 1.

Fig. 4. Effect of heating rate on peak temperature: ———, initial temperature; ————, maximum temperature; ······, final temperature.

thereby to be in the range 182–212°C, as shown in Fig. 4. The maximum temperature of a reaction peak is usually considered as the temperature at which the reaction proceeds most violently; thus, the optimal value would be about 202°C. The isothermal TG experiments in the above temperature range were made to further the search for optimum conditions. According to the conditions nos. 4–6 in Table 1, light yellow products are obtained, the IR spectra of which are consistent with that of standard BTDA, and the DSC curves of which exhibit an identical sharp and very regular endothermic peak (Fig. 5(a)). It follows that the selected conditions can be used to prepare BTDA of higher purity.

TABLE 1

Isothermal thermogravimetric measurements

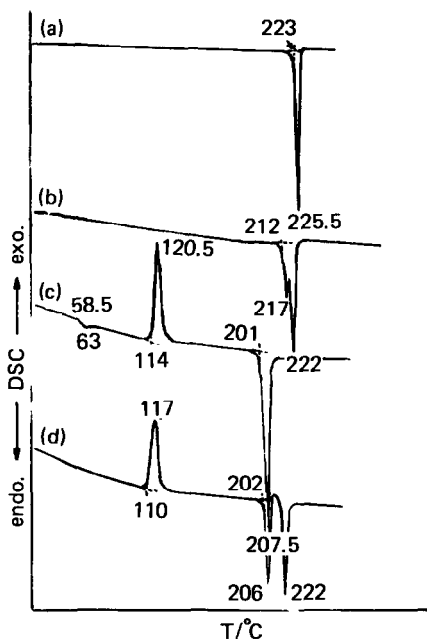| No.	Sample mass (mg)	Temperature (°C)	Time (min)	Mass loss (%)
1	15.07	186	240	5.97
2	15.12	190	224	8.33
3	15.03	195	164	8.98
4	15.15	198	130	9.97
5	15.05	203.5	60	9.50
6	15.12	211	30	9.92

Fig. 5. DSC curves of BTDA prepared from BTA by various procedures: (a) 190–195 °C, 2 h, 44 min; (b) in oven, 240 °C, 3 h; (c) heating to 275 °C at 10 °C min⁻¹ and slow cooling; (d) heating to 275 °C at 10 °C min⁻¹ and rapid cooling.

It is reported that BTDA can be prepared by the heat dehydration of BTA in the melting state. In general, BTA is subjected to dehydration at 227–228 °C for 15–20 min, then cooled rapidly; consequently BTDA is obtained.

BTA is heated to 275 °C in air, i.e. the dehydration–melting peak just ends, and then the sample is cooled to room temperature either rapidly or slowly. In the DSC curves of the product from rapid cooling an exotherm at 117 °C and an endotherm at 206 °C appear in addition to the melting peak (Fig. 5(d)). Compared with pure BTDA, the bands in its IR spectrum at 1725, 1046 and 928 cm⁻¹ disappear, a new band appears at 830 cm⁻¹ and the bands at 980, 920 and 890 cm⁻¹ become stronger. It is believed that high temperature causes BTDA to degrade in some measure. In the DSC curves of the product from slow cooling, there occur a small endotherm at 63 °C, an exotherm at 120.5 °C, and endotherms at 207.5 °C and 210.5 °C. No melting peak of BTDA is observed (Fig. 5(c)). This indicates that samples held at high temperature for a long time will degrade significantly. BTDA obtained by heating BTA at 240 °C in an oven for 3 h yields a DSC peak of impurity at 217 °C (Fig. 5(b)) and an IR spectrogram distinct from that of pure BTDA.

When the dehydration reaction takes place under reduced pressure (about 10 mmHg), the peak temperature for dehydration in DSC is lower than that
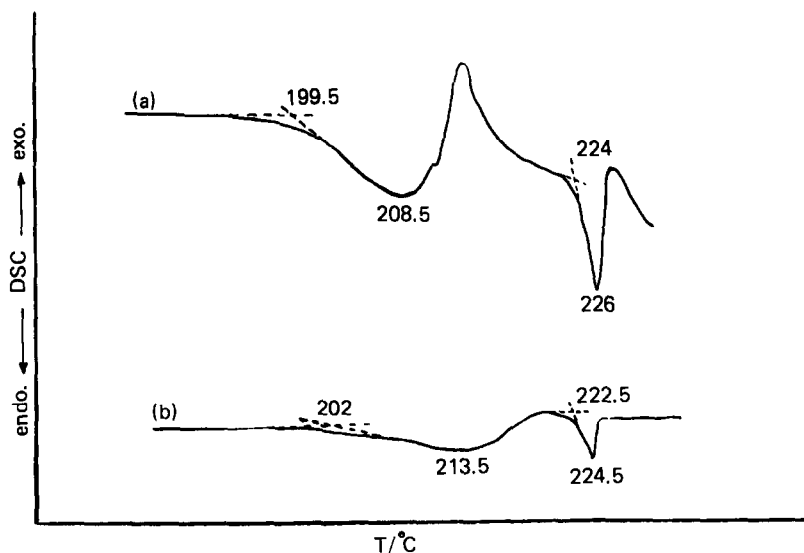
Fig. 6. Comparison between dehydration under (a) ordinary pressure and (b) reduced pressure.

under atmospheric pressure (see Fig. 6), so decreasing pressure is advantageous to the dehydration of BTA.

In a stream of high pure nitrogen, BTA is heated to the end of the dehydration–melting endotherm, followed by slow cooling to room temperature. For the product prepared by this means, the DSC curve in air (Fig. 7(a)) displays a small endotherm at 64°C, an exotherm at 160°C and an endotherm at 210.5°C; this is analogous to Fig. 5(c). However, the DSC curve in nitrogen displays only the small endotherm at 63°C; there is no melting of BTDA, nor peaks corresponding to those at 160 and 210.5°C (Fig. 7(b)). These phenomena clearly show that the extent of degradation of BTDA chiefly depends on the temperature and scarcely bears any relation to the atmosphere. It is possible that the exotherm and endotherms which are observed in DSC in air but not in nitrogen arise from reactions between degradation products and oxygen.

BTDA prepared by controlled dehydration in the optimum temperature range has a regular melting peak of 226°C in its DSC curve in nitrogen (Fig. 7(c)).

From the above it is evident that when the temperature is above its melting point, BTDA degrades significantly yielding some coloured compounds. If it is kept at high temperature for a long time, it partly decomposes and changes from light yellow to light brown and thence to dark brown. The multipeak phenomenon would appear in the thermal analysis curves. Usually, such products are difficult to purify satisfactorily either by means of recrystallization or decolourization.
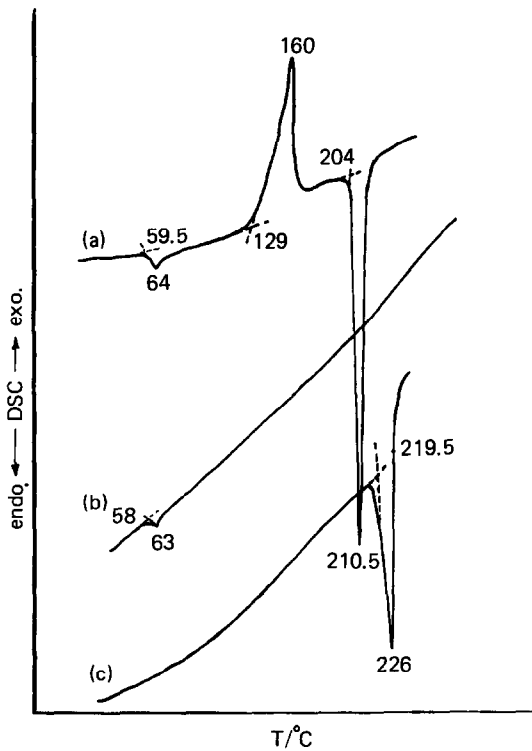
Fig. 7. Effect of atmosphere on dehydration of BTA: (a) and (b) sample obtained by heating to 270°C in N_2, DSC in air (a) and N_2 (b); (c) sample obtained by heating at 198°C for 2 h, DSC in N_2.

Dehydration kinetics

The overall rate equation of a chemical reaction may be frequently expressed as

$$dX/dt = Kf(X) \tag{1}$$

where X is the fraction of material reacted, t is the reaction time, K is the specific rate constant, and $f(X)$ is some function describing the reaction mechanism.

Integrating eqn. (1) yields

$$F(X) = Kt + C \tag{2}$$

where $F(X)$ is the expression of $\int_0^X dX/f(X)$ and C is an integral constant.

According to the conventional method, the experiments are carried out under isothermal conditions to acquire the relation of X versus t; then the values of X and corresponding t are respectively substituted into each of the rate equations which are derived from some potential reaction mechanisms. If a plot of $F(X)$ versus t exhibits a linear relation, then $F(X)$ is considered

TABLE 2

List of kinetic equations examined in this study

Symbol	$F(X)$	Model
A4	$[-\ln(1-X)]^{1/4}$	Random nucleation and the growth of nuclei ($n = 4$)
A3	$[-\ln(1-X)]^{1/3}$	Random nucleation and the growth of nuclei ($n = 3$)
A2	$[-\ln(1-X)]^{1/2}$	Random nucleation and the growth of nuclei ($n = 2$)
R2	$1-(1-X)^{1/2}$	Two-dimensional phase boundary reaction
R3	$1-(1-X)^{1/3}$	Three-dimensional phase boundary reaction
F1	$-\ln(1-X)$	Random nucleation
D1	X^2	One-dimensional diffusion
D2	$X+(1-X)\ln(1-X)$	Two-dimensional diffusion
D3	$[1-(1-X)^{1/3}]^2$	Three-dimensional diffusion (Jander equation)
D4	$1-2/3X-(1-X)^{2/3}$	Three-dimensional diffusion (Ginstiling–Brounshtoi equation)

as a potential mechanism model. The value of K is given from the slope of the straight line, which follows the Arrhenius equation

$$K = A \exp(-E/RT) \tag{3}$$

where A is the pre-exponential factor, E is the activation energy, T is the absolute temperature and R is the gas constant. If eqn. (3) is rewritten in logarithmic form

$$\ln K = \ln A - E/RT \tag{4}$$

plotting $\ln K$ versus $1/T$ gives a straight line, whose slope is $-E/R$ and intercept is $\ln A$.

The kinetic models which are often used for solid-state decomposition reactions and which are examined in this study are listed in Table 2.

By application of the above method, the respective plots of $F(X)$ versus t are drawn for each model. The model which has the best linear relationship, i.e. the correlation coefficient closest to unity, is selected. However, as can be seen from Table 3, the differences between the correlation coefficients for some models would be very small. Furthermore, the models chosen from the data obtained for the various dehydration temperatures would not be the same. For this reason, it seems inappropriate for the correlation coefficient to be the entire basis of discrimination between models.

Therefore we pretreat each model by use of this method, and take the preliminary results obtained as the initial values of a sequential procedure for discrimination between the rival models.

TABLE 3

Correlation coefficient for each model at various temperatures

Model	Correlation coefficient of $F(X)$ versus t			
	209.8°C	207.4°C	203.8°C	201.5°C
A4	0.9329	0.9434	0.9266	0.9472
A3	0.9702	0.9738	0.9619	0.9772
A2	0.9953	0.9951	0.9883	0.9945
R2	0.9966	0.9954	0.9919	0.9885
R3	0.9991	0.9943	0.9918	0.9853
F1	0.9780	0.9806	0.9876	0.9750
D1	0.9867	0.9855	0.9811	0.9656
D2	0.9917	0.9781	0.9743	0.9529
D3	0.9991	0.9943	0.9918	0.9853
D4	0.9881	0.9707	0.9701	0.9461
Better models	R3, D3	R2	R2	A2

The sequential procedure is based upon probability and information theory. In this approach each model is tested statistically and its behaviour is judged by a comprehensive analysis of the following statistical parameters: π (the probability of the model), ρ^2 (the experimental complex correlation coefficient), F (the ratio of the mean square for regression to the mean square of calculation error for the model), F_E (the ratio of the mean square of calculation error for the model to the variance for experiment error). If the posterior probability of a model is much less than that of the others, it would be rejected; however, if one of the models shows absolute dominance, the discrimination can be ended [3]. Therefore, the discrimination of viral models by this sequential procedure has certain characteristics and often has advantages over the other usual method. We have reported the application of this procedure to kinetic analysis on the basis of DTA data [4]. In this study, it is applied to isothermal TG data. The concrete practice is briefly described as follows.

The experimental data from four temperatures are mixed and grouped to eliminate the effect of temperature on the discrimination of models. The grouped data are used as elemental and additional experimental points, respectively. The discrimination is carried out on a microcomputer Z-80 through a sequential procedure program. Because of the limited storage capacity of the microcomputer, only eight models can be discriminated in a run. Therefore, ten models to be examined are divided into two groups. The first group consisted of the following six models: A4, A2, R2, F1, D1, D2 (see Table 2). Two better models, R2 and D1, are yielded by the first calculation run. Then, the additional experimental points are added and computed, which are chosen by computer in such a manner that enables the difference between models to become the largest. As a consequence, D1 is chosen as a best fitting model. The better models from the first group and

the remaining models without being discriminated are classed as the second group, which hence includes D3, A3, D4, R2, R3 and D1. The sequential discrimination is repeated again. Finally, D1 is still optimal. From this we conclude that the dehydration of BTA follows a one-dimensional diffusion mechanism and can be described by the equation

$$X^2 = A \exp(-E/RT)t$$

where $E = 135.5$ KJ mol^{-1} and $A = 2.49 \times 10^{12}$ min^{-1}. The overall reaction rate is controlled by the diffusion rate in which the vapour produced during the dehydration passes through the phase boundary. Thus, diminishing the reaction pressure or increasing the flow rate of inert gas would increase the dehydration rate due to diffusion being favoured and removal of water formed during the reaction.

REFERENCES

1 J.G.D. Schulz and A. Onopchenko, Ind. Eng. Chem., Prod. Res. Dev., 15(2) (1976) 152.
2 M.I. Farberov, Idr., Dokl. Akad. Nauk. SSSR, 178(6) (1968) 1348.
3 Wu Xijun, Huang Zixing, Zhao Zhiliang and Liu Deming, J. Chem. Ind. Eng. (China), 2 (1979) 133.
4 Ye Su, Zhou Dezhen and Ran Quanyin, Acta Physicochim. Sin., 2(5) (1986) 392.